732. *Germanium Esters. Part II.*[1] *Intermolecular Forces and Liquid Structure.*

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Vapour pressures and viscosities have been measured over a range of temperatures for germanium esters $Ge(OR)_4$ where R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, and Bu^t. Energies and entropies of vaporisation have been calculated, together with energies and entropies of activation for viscous flow. The behaviour of germanium esters in the liquid state is discussed.

In Part I[1] were reported the densities and surface tensions of some germanium esters over a range of temperature. An analysis of their parachors suggested that germanium esters are forced, by the configuration of the alkyl group, to adopt certain preferred conformations in the liquid. For example, in the straight-chain *n*-alkyl derivatives it appears that the four $^-$OR chains are disposed in two parallel pairs inclined approximately at right angles to a common axis passing through the germanium atom; the molecule, by rotation about the long axis, can assume a roughly cylindrical shape. In the branched-chain esters this conformation is prevented by intramolecular congestion and a disc-like conformation is preferred. In an attempt to throw further light on this problem we systematically studied other physical properties of germanium esters and now report measurements of vapour pressures and viscosities over a range of temperatures.

Experimental

Germanium Esters.—These were prepared as described in Part I.[1]

Vapour Pressures.—Boiling points were measured under reduced pressure of dry nitrogen in an all-glass apparatus similar to the one used in earlier work on metal alkoxides and silicon esters.[2] Measurements for each ester were made on two different samples (*ca.* 5 c.c.), first in order of ascending pressures and then the reverse. During a " run " small fractions were distilled out at various temperatures and the boiling points rechecked. This procedure ensured that no volatile impurities were present. Pressures in the range 5—200 mm. Hg were measured

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[1] Part I, Bradley, Kay, and Wardlaw, *J.*, 1956, 4916.

[2] Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 5020; Bradley, Mehrotra, Swanwick, and Wardlaw, *J.*, 1953, 2025.

on a conventional mercury manometer with a travelling microscope. For each compound the results conformed to the simple equation $\log P_{\text{mm.}} = a - b/T$, and the values of a and b are given in Table 1.

Viscosities.—An all-glass viscometer of the Ostwald type was constructed with standard joints and vacuum taps to enable the sample to be distilled in directly under reduced pressure. Atmospheric moisture was rigorously excluded and measurements were made under dry nitrogen on two separate samples of each ester. The apparatus was calibrated at various temperatures between 20° and 45° with benzene and no significant variation of the apparatus constant was found. The viscometer was immersed in a thermostat ($\pm 0{\cdot}1°$) for at least 1 hr. at each temperature to attain thermal equilibrium. Measurements were then made in the following sequence of temperatures: 20°, 25°, 30°, 35°, 40°, 45°, 42·5°, 37·5°, 32·5°, 27·5°, and 22·5°. The esters exhibited Newtonian flow and in each case the results conformed to the simple equation $\log \eta$ (millipoises) $= c/T - d$, and the values of c and d are given in Table 1.

TABLE 1.

R in Ge(OR)$_4$	a	b	c	d	R in Ge(OR)$_4$	a	b	c	d
Me	8·28	2300	346·5	0·294	Bu^n	8·58	3260	671·0	0·929
Et	8·33	2500	463·8	0·559	Bu^i	8·79	3130	782·6	1·222
Pr^n	8·47	2870	575·7	0·787	Bu^s	8·88	3130	812·8	1·325
Pr^i	8·76	2865	567·1	0·816	Bu^t	8·41	2810	1227·8	2·368

DISCUSSION

Boiling Points and Heats and Entropies of Vaporisation.—In Table 2 are presented the boiling points under 5 mm. pressure ($T_{5\cdot0}$) and the molar heats of vaporisation (ΔH_v, in kcal./mole). The increment in boiling point (ΔT) in ascending the homologous series of *n*-alkyl orthogermanates is also given in addition to the entropies of vaporisation at 5 mm. pressure ($\Delta S_{5\cdot0}$, cal./deg./mole). Because it is generally accepted that a comparison of entropies of vaporisation of different compounds at the same pressure may be misleading if these compounds have appreciably different boiling points, we have adopted Hildebrand's [3, 4] method of comparing entropies at the same molar concentration of vapour. Stavely and Tupman [5] have recently extended and refined Hildebrand's treatment but we have not sufficient data (*e.g.*, critical constants) to apply their method. The values for the " Hildebrand entropy " ΔS_H (cal./deg./mole) in Table 2 were calculated for a vapour concentration of 0·00507 mole/l. Some data on silicon esters [2] determined under similar conditions are also included for comparison.

TABLE 2.

R in Ge(OR)$_4$	$T_{5\cdot0}$	ΔT	ΔH_v	ΔS_v	ΔS_H	R in Ge(OR)$_4$	$T_{5\cdot0}$	ΔH_v	ΔS_v	ΔS_H
Me	30·0°	—	10·5	34·7	28·4	Bu^s	109·5°	14·3	37·4	30·7
Et	54·4	24·4	11·4	34·9	28·5	Bu^t	91·5	12·9	35·3	28·6
Pr^n	96·3	41·9	13·1	35·5	28·9	Si(OEt)$_4$ ...	42·1	11·2	35·5	29·3
Bu^n	140·2	43·9	14·9	36·0	29·1	Si(OPr^i)$_4$ ...	55·8	11·2	34·0	30·2
Pr^i	82·0	—	13·1	36·9	30·3	Si(OBu^n)$_4$...	123·4	14·8	37·4	30·6
Bu^i	113·4	—	14·2	36·7	30·0					

As a basis for comparison with the germanium esters we present in Table 3 some " Hildebrand entropies " for simpler molecules calculated from Hildebrand's [3] results.

TABLE 3.

Compound	N_2	O_2	CCl_4	$SnCl_4$	C_6H_6	Zn	Cd	Hg
ΔS_H	27·4	27·4	26·8	27·0	27·2	26·2	26·2	26·0

Apart from the metals, these compounds have $\Delta S_H \simeq 27$. Stavely and Tupman [4] consider that the diatomic molecules N_2 and O_2 are not freely rotating because they have entropies of vaporisation which are high relative to values deduced from a reference curve

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[3] Hildebrand, *J. Amer. Chem. Soc.*, 1915, **37**, 970.

[4] *Idem, J. Chem. Phys.*, 1939, **7**, 233.

[5] Stavely and Tupman, *J.*, 1950, 3600.

of ΔS against $10^3P/T$. However, this is based mainly on mercury as a substance exhibiting unrestricted rotation and we are not convinced that mercury is an appropriate standard substance because of its metallic properties, and especially as the inert gases have higher entropies of vaporisation, and it seems improbable that mercury atoms could have freer rotation than atoms of inert gases. Accordingly we suggest $\Delta S_{\mathrm{H}} = 27$ as a good value for a liquid whose molecules exhibit substantially free rotation.

It is clear that all of the substances listed in Table 2 have anomalously high ΔS_{H}'s.

Internal Energy of Vaporisation and Molar Work of Cohesion.—Grunberg and Nissan [6] have discussed the structural implications for simple organic molecules of the energy relationships involved in vaporisation, viscous flow, and surface formation. They derived the following molar work of cohesion: $W_{\mathrm{c}} = 2\gamma \boldsymbol{N}^{1/3}V_{\mathrm{l}}^{2/3}$, where γ is the surface tension and V_{l} the molar volume of the liquid. The energy per mole to overcome intermolecular attraction in the liquid is given by the internal energy of vaporisation, $E_{\mathrm{v}} = \Delta H_{\mathrm{v}} - P(V_{\mathrm{g}} - V_{\mathrm{l}})$ where V_{g} is the molar volume of the vapour. The approximation $E_{\mathrm{v}} = \Delta H_{\mathrm{v}} - \boldsymbol{R}T$ may also be used. Grunberg and Nissan [6] consider a liquid to have a statistical structure with each molecule generally surrounded by n nearest neighbours and the intermolecular forces localised in "bonds" between nearest neighbours. They suggested that in surface formation the energy required is determined by the smallest number of "bonds" which must be disrupted to expose the central molecule and that this is related to the geometrical configuration of the n nearest neighbours. In this manner they deduced that for hexagonal (close-packed), cubic (close-packed), cubic (body-centred), octahedral, and tetrahedral configurations the ratio $E_{\mathrm{v}}/W_{\mathrm{c}}$ would be 4, 4, 4, 3, and 2 respectively. Hence the ratio $E_{\mathrm{v}}/W_{\mathrm{c}}$ can be used to determine the configuration of molecules in the liquid. We have derived values of E_{v} and W_{c} for the germanium esters and the results are given in Table 4. These figures relate to 40° and it is assumed that the latent heats quoted in Table 2 are applicable. Values of W_{c} were calculated from the surface tensions and densities published earlier.[1]

TABLE 4.

R in $Ge(OR)_4$	E_{v}	W_{c}	$E_{\mathrm{v}}/W_{\mathrm{c}}$	$E_{\mathrm{visc.}}/W_{\mathrm{c}}$	$E_{\mathrm{v}}/E_{\mathrm{visc.}}$	R in $Ge(OR)_4$	E_{v}	W_{c}	$E_{\mathrm{v}}/W_{\mathrm{c}}$	$E_{\mathrm{visc.}}/W_{\mathrm{c}}$	$E_{\mathrm{v}}/E_{\mathrm{visc.}}$
Me	9·9	2·43	3·8	0·64	6·2	Pr^i	12·5	3·56	3·5	0·73	4·8
Et	10·8	3·30	3·3	0·64	5·1	Bu^i	13·6	4·55	3·0	0·79	3·8
Pr^n	12·5	4·00	3·1	0·66	4·8	Bu^s	13·7	4·54	3·0	0·82	3·7
Bu^n	14·3	4·66	3·1	0·66	4·6	Bu^t	12·2	4·32	2·7	1·30	2·1

Viscous Flow.—Following Eyring's [7] treatment of the theory of viscous flow we have calculated activation energies ($E_{\mathrm{visc.}}$, kcal./mole), free energies of activation ($\Delta F^{\ddagger}$, kcal./mole) and entropies of activation ($\Delta S^{\ddagger}$, cals./deg./mole) for viscous flow for the germanium esters. To illustrate the small effect of temperature on $\Delta F^{\ddagger}$ and $\Delta S^{\ddagger}$ we include in Table 5 data at 20° and 40° (except for the *tert.*-butyl ester, m. p. 23·5°).

TABLE 5.

R in $Ge(OR)_4$	Temp.	η (mP)	$E_{\mathrm{visc.}}$	$\Delta F^{\ddagger}$	$\Delta S^{\ddagger}$	R in $Ge(OR)_4$	Temp.	η (mP)	$E_{\mathrm{visc.}}$	$\Delta F^{\ddagger}$	$\Delta S^{\ddagger}$
Me	20°	7·73	1·58	3·29	−5·8	Pr^i	20°	13·15	2·59	4·01	$-4{\cdot}8_5$
	40	6·49		3·42	−5·9		40	9·90		4·12	−4·9
Et	20	10·57	2·12	3·71	−5·4	Bu^i	20	28·10	3·58	4·56	−3·3
	40	8·36		3·83	−5·5		40	18·90		4·64	−3·4
Pr^n	20	15·10	2·63	4·07	−4·9	Bu^s	20	28·10	3·72	4·55	−2·8
	40	11·25		4·18	$-4{\cdot}9_5$		40	18·60		4·62	−2·9
Bu^n	20	21·90	3·07	4·41	−4·6	Bu^t	(25)	(56·35)	5·62	(5·03)	(+2·0)
	40	15·95		4·53	−4·7		40	35·70		5·01	+2·0

Values for $E_{\mathrm{v}}/E_{\mathrm{visc.}}$ and $E_{\mathrm{visc.}}/W_{\mathrm{c}}$ are included in Table 4. We now discuss the structural implications of the data given in Tables 2, 4, and 5.

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[6] Grunberg and Nissan, *Trans. Faraday Soc.*, 1949, **45**, 125.

[7] Eyring, *J. Chem. Phys.*, 1936, **4**, 283; also Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, 1941.

n-Alkyl Orthogermanates.—The series from methyl to *n*-butyl shows the expected increase in b. p. and in the energy parameters ΔH_v, W_c, and $E_{visc.}$ with increase in size of the molecule. The values of ΔS_H increase slightly in ascending the series but this is barely significant against a probable error of *ca.* $\pm 0{\cdot}3$ unit. On the other hand, $\Delta S^\ddagger$ becomes steadily less negative from methyl to *n*-butyl and it is noteworthy that Moore, Gibbs, and Eyring [8] showed that in the normal alkanes from C_5 to C_{64} $\Delta S^\ddagger$ becomes more negative. The methyl ester appears " anomalous " in some respects. Thus ΔT from methyl to ethyl is much smaller than succeeding increments and the same applies to increments in ΔH_v, suggesting that intermolecular forces are abnormally high in the methyl ester. However, the entropy of vaporisation reveals no significant difference between the methyl ester and the higher homologues whilst for W_c and $E_{visc.}$ the increments become smaller in ascending the series. The " high " value for ΔH_v (and E_v) for the methyl ester is further reflected in the methyl ester's having abnormally large values for E_v/W_c and $E_v/E_{visc.}$ compared with the higher homologues. Grunberg and Nissan's [6] theory being applied, the high value for E_v/W_c suggests that the methyl ester has a higher " co-ordination number " in the liquid state than the other homologues. This is reasonable in view of the methyl ester's being smaller than the others and more nearly spherical in shape, and hence capable of achieving a higher symmetry in the liquid. This view is supported by the high value of $E_v/E_{visc.}$ if we apply Moore, Gibbs, and Eyring's theory.[8] They suggest that straight-chain hydrocarbons behave as quasi-crystalline liquids in which the mechanism of flow involves a co-operative movement analogous to the flow of metals by movement of dislocations in the crystal lattice and resulting in values of $E_{visc.}$ small relative to E_v. On this basis the high value of $E_v/E_{visc.}$ for methyl orthogermanate indicates a high degree of " quasi-crystallinity " in the liquid with flow by the co-operative mechanism. Increase in the length of the *n*-alkyl chain in the germanium esters lowers the symmetry (and quasi-crystallinity) and reduces the scope for flow by the co-operative mechanism.

Branched-chain Alkyl Orthogermanates.—The expected effect of chain branching on intermolecular forces and volatility is shown by the boiling points and heats of vaporisation of the isomeric butyl orthogermanates (Table 2). The ΔS_H's are all greater than 27 e.u. and it appears that even the tertiary isomer exhibits restricted molecular rotation. The energies of vaporisation (E_v) and works of cohesion (W_c) show parallel trends: $Bu^n > Bu^i \simeq Bu^s > Bu^t$, and, except for Bu^t, the ratio E_v/W_c is 3, suggesting an octahedral configuration in the liquid. The most striking feature of these results is the fact that E_{visc} shows an exactly opposite trend to E_v or W_c. This causes the ratio $E_v/E_{visc.}$ to fall rapidly in the order $Bu^n > Bu^i > Bu^s > Bu^t$ and suggests a change in mechanism of flow as the alkyl groups become more branched. In fact Moore *et al.*[8] suggested that for complex molecules having a low order of quasi-crystallinity and exhibiting restricted rotation the co-operative mechanism of flow could not operate and flow would involve molecular " jumps ". Moreover, they postulated for flow by molecular jumps that the ratio $E_v/E_{visc.}$ would be nearly 2 and $\Delta S^\ddagger$ positive. This is indeed the case for the *tert.*-butyl isomer and it appears that in changing from Bu^n to Bu^i to Bu^s to Bu^t the mechanism of flow changes from the co-operative phenomenon to that of individual molecular jumps. In line with this we note that $\Delta S^\ddagger$ becomes steadily more positive from Bu^n to Bu^t. The suggestion of less quasi-crystalline structure in the *tert.*-butyl ester is also supported by its low value for E_v/W_c. This postulated change in symmetry or quasi-crystallinity from Bu^n to Bu^t is also in accord with our suggestions for the preferred conformations of these esters based on analysis of their parachors. Thus the cylindrical molecules of the *n*-butyl ester can pack together to a certain degree but branching of the alkyl chains interferes with this packing.

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[8] Moore, Gibbs, and Eyring, *J. Phys. Chem.*, 1953, **57**, 172.